

REMARKS

The Office Action of May 2, 2002 has been carefully considered.

Upon review of the application as filed, it was determined that portions of the original French application were incorrectly translated, and this incorrect translation resulted in unclear claim language. Due to the numerous changes necessary to clarify the specification, Applicant believes that a substitute specification is the best way to make the necessary corrections. A substitute specification in clean and marked-up forms therefore accompanies this amendment. No new matter is thought to be added in this substitute specification.

Entry of the substitute specification is requested.

Claims 1-6 have been rejected under 35 USC 112, 2nd paragraph on a number of grounds. These claims have now been canceled and replaced by new claims 7-14.

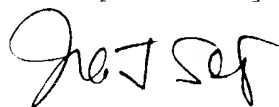
Claims 7-12 correspond to canceled claims 1-6. Claim 13 recites subject matter disclosed in the substitute specification (clean copy) at page 7, line 9 through page 8, line 9, and claim 14 recites subject matter disclosed in the substitute specification (clean copy) at page 9, line 32 through page 10, line 20.

Applicant submits that the objections raised in the

Office Action relating to unclear terminology and lack of antecedent basis have been obviated by the submission of the substitute specification and new claims 7-14, and withdrawal of this rejection is requested.

In view of the foregoing amendments and remarks, Applicants submit that the present application is now in condition for allowance. An early allowance of the application with amended claims is earnestly solicited.

Respectfully submitted,



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PROCESS FOR CONTROLLING THE PARTICLE SIZE IN A BAYER
CIRCUIT PRECIPITATION SYSTEM, INCLUDING AN
AGGLOMERATION PHASE

Technical domain

The invention relates to the precipitation of alumina trihydrate according to the Bayer process, carried out in an American type precipitation system including a preliminary agglomeration phase.

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State of prior art

The Bayer process can produce alumina from bauxite ore, particularly alumina designed to be transformed
10 into aluminum by igneous electrolysis. According to this process, the bauxite ore is treated when hot by means of an aqueous sodium hydroxide solution with an appropriate concentration in order to obtain a suspension containing pregnant sodium aluminate liquor
15 and insoluble residues. After separation of these residues, the pregnant sodium aluminate liquor, also called Bayer liquor, is decomposed by seeding with recycled aluminum trihydroxide particles until aluminum trihydroxide grains (also called alumina trihydrate or
20 hydrargillite) are obtained, and which are themselves then calcinated to obtain an alumina with particular particle size distribution and physicochemical properties. The sodium aluminate liquor depleted in alumina (spent liquor) is then recycled to digest the
25 ore, possibly after being concentrated, by the evaporation and addition of sodium hydroxide or caustic soda.

The productivity of the liquor during its crystallisation is defined by the quantity of alumina restored in the form of alumina trihydrate by crystallisation of the pregnant liquor, related to a given volume of pregnant liquor. The productivity expressed in kilograms of alumina per cubic meter of liquor ($\text{kg of Al}_2\text{O}_3/\text{m}^3$), is related to the caustic concentration in the pregnant liquor. In general, this concentration in American type Bayer processes is close to 100-130 g of Na_2O / liter, which is lower than in European type Bayer processes, and this explains why a productivity in the crystallisation of the pregnant liquor is considered to be good when it exceeds 70 $\text{kg of Al}_2\text{O}_3/\text{m}^3$ for an American type Bayer process, or when it exceeds 80 $\text{kg of Al}_2\text{O}_3/\text{m}^3$ for a European type Bayer process.

The difference between European type and American type Bayer processes is in the solid content of the slurry during precipitation. The slurry is the result of introducing a recycled alumina trihydrate seed into the aluminate liquor, and part of the alumina in solution changing to the solid phase. We will define the solid content in the slurry as the weight of solid particles present in the slurry per unit volume of pregnant aluminate liquor entering into the precipitation workshop (and not per unit volume of the suspension).

Alumina to be transformed into aluminum by igneous electrolysis must have a number of properties, including:

- good so that electrolysis tanks can be continuously supplied with controlled quantities of alumina,

- a high dissolution rate,
- a low tendency to dusting.

These properties are closely related to the morphology and the particle size distribution of alumina grains, themselves closely related to the morphology and particle size distribution of hydrargillite particles formed during the precipitation. It is particularly important to limit the proportion of very fine particles that can be classified in two main categories: fines (for which the average diameter is between 10 and 50 μm) and ultrafines, for which the average diameter is less than 10 μm . Since a good correlation is observed between the particle size distribution of alumina and the particle size distribution of the production hydrate from which it is derived, an attempt is made to control the particle size of the

in the precipitation series, and particularly in the crystal growth phase. Thus for example, in order to obtain a good quality "metallurgical" alumina,

hydrate for which the amount passing a 45 μm sieve is less than 10%, a suspension containing less than 10% of particles with a diameter of less than

In the rest of this discussion, we will denote the passing X micrometers

as "%<X".

Concerning the American type Bayer process, the precipitation comprises a preliminary agglomeration phase characterized by a particularly low solid content. In patent US 4 234 559, the precipitation

circuit comprises firstly a series of agglomeration tanks and then a series of feed tanks and finally three classification tanks (primary, secondary, tertiary). While the hydrate produced is derived from the underflow from the primary classification tank, the fines seed originating from the underflow from the tertiary classification tank is inserted in controlled quantities into the series of agglomeration tanks and the larger seed originating from the underflow from the secondary classification tank is added into the series of feed tanks. Since the fines are destroyed during the agglomeration phase, the problem of controlling the particle size of the hydrate produced does not arise.

But attempts are being made to increase the productivity of the American type Bayer process, which is lower than the productivity of European type Bayer cycles. In US 5 158 577 and EP 0 515 407, only part of the pregnant liquor is added into the agglomeration and the rest is added directly to the

different solid contents in these two parts of the crystallization

in agglomeration tanks which is essential if it is required that agglomeration should take place under good conditions, and a high solid content in feed

But an instability in the precipitation is observed if the content is increased at the and if the number of agglomeration tanks is limited, with a serious risk of the sudden appearance of large quantities of fines in

The particle size instability is due to a reduction in the ratio between the sum of the production and the fine seed sent to the fine seed separator.

A reduction in this ratio makes it impossible to implement effective corrective actions when a drift in the process is observed on the \bar{x} chart. This is especially true for the hydrate.

Statement of the problem

Therefore, the applicant attempted to define a process that could increase the productivity of the American type Bayer process by preventing unacceptable particle size fluctuations, particularly the sudden appearance of large quantities of fines and ultrafines in the hydrate.

Purpose of the invention

The process developed by the applicant is a process for controlling the precipitation of an American type Bayer circuit including a preliminary agglomeration phase, a crystal growth phase and a classification phase, in which the particle size quality of the hydrate produced is monitored by measuring

characterized in that it comprises:

- a) a preparation step carried out once and for all,
intended firstly to setup a relation R in
intensity and in time between

X_2 μm , where X_1 is than X_2 ,
and secondly to define trigger thresholds on the
value of X_1 μm , starting
from the maximum authorized variation interval
on X_2 μm ;

- b) control of the process itself, carried out
during the installation operating period which,
apart from the daily measurement of X_2 μm and a regular update of the
correlation between the said X_2 μm and the particle size of the
hydrate produced, a daily measurement of the

X_1 μm and a regular update of the relation R
between X_1 μm
and X_2 μm ,
and triggering of corrective action in the
slurry at the beginning of the precipitation
when the measured value of
 X_1 μm reaches one of the regularly updated
trigger thresholds determined in the previous
step.

This corrective action in the slurry at the
beginning of precipitation may be a modification to the
temperature of the aluminate liquor added into the
agglomeration tank, the addition of additives at the

beginning of the crystal growth system such as "Crystal Growth Modifiers" described in US 4 737 352, recycling a part of the end of

slurry, or preferably, modification of the solid
5 content in the slurry in the first agglomeration tank.

The solid content in the slurry in the agglomeration phase may be modified simply by adding more or less pregnant aluminate liquor in the first agglomeration tank, the remaining aliquot being
10 directed to the feed tank. If

$X_1 \mu\text{m}$ is too great, there are too many fines; the amount of pregnant aluminate liquor fed into the agglomeration tank must be increased. If

$X_1 \mu\text{m}$ is too low, there is a risk
15 that productivity will be reduced. If the amount of pregnant aluminate liquor fed into the agglomeration tank is reduced.

The preliminary step, carried out once only, is intended to determine the relation R and trigger
20 thresholds for the values of $X_1 \mu\text{m}$ that will be used at the beginning of application of the process control. This preliminary step comprises the following steps:

a1) Daily measurement of $X_1 \mu\text{m}$
25 in the slurry at a particular point in the precipitation system, which is used to produce a first particle size time diagram represented by a curve $Y = \%<X_1(t)$.

a2) Daily measurement $X_2 \mu\text{m}$
30 in the slurry at a particular point in the precipitation system, which is used to produce a second particle size time diagram represented by a curve $Y = \%<X_2(t)$ and in which X_2 , greater than X_1 , is a value already known for its good

correlation with the particle size of the hydrate produced. For example, it may be 45 μm measured in slurry at

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- a3) Creation of an empirical relation between the two particle size time diagrams, the purpose of which is to characterize the relation between the variation of X_1 μm and the variation of X_2 μm , in intensity and in time. This relation R may be written in the form:

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$$R(\%X_2(t), \%X_1(t-\tau)) = 0$$

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where t is the date on which X_2 μm is measured and τ is a characteristic time interval estimated by observing the occurrence of the same accidental phenomenon on each curve (the same type of extreme, an inflection, etc.).

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- a4) Definition of the maximum threshold and the minimum threshold of X_1 μm , obtained from the relation R previously established and a maximum interval of the authorized variation of values of X_1 μm .

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The purpose of the relation R is to predict the variation in the particle size, in other words to anticipate crises, by observing the variation in the population of the finest hydrate particles

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a size of less than X_1 μm). The applicant observed that

an accident on the time diagram $\%X1(t)$ is amplified and shifted in time on the $\%X2(t)$ time diagram. The
 5 time shift " τ " is higher as the difference between $X1$ and $X2$ increases. In practice, a value $X2$ greater than 40 μm (normally 45 μm) will be chosen, and the value of $X1$ will be taken to be less than or equal to 20 μm .

The measurement point is preferably at \dots ,
 10 \dots but it may take place earlier, provided that it remains within the \dots series. Measurement points for

\dots may be different. However, they
 15 must remain the same throughout the process control and must be as far as possible from the points at which disturbing additions are made irregularly in the slurry.

Measurements referred to as being "daily" are
 20 regular measurements and although they are not necessarily daily, they are sufficient frequent to give useable time diagrams.

Concerning the required variation interval of
 $X2 \mu\text{m}$, a maximum is defined above
 25 which it is known that the particle size of the hydrate produced is no longer satisfactory (too many fines) and a minimum is defined below which it is known that economic operating conditions become bad.

The trigger thresholds are thus determined from the
 30 time diagram for $X1 \mu\text{m}$, taking account not only of the maximum authorized variation interval on the values of $X2 \mu\text{m}$, but also the uncertainty of the measurement of \dots

X1 μm and the stability of the efficiency of the hydrate classification system.

This preparatory step, at the end of which the time diagrams, the relation R and the trigger threshold become operational, is of the order of three months. But this step can be accelerated either by deliberately triggering an excess creation of fines, or by analyzing previous particle size results if they contain the required information about

X2 μm .

Since precipitation is a complex phenomenon that depends on a large number of parameters (particularly the composition of the treated bauxite that may change in time), instead of using a relation R established once and for all, it is better to use a relation that is regularly updated. Similarly, the correlation between the value of X2 μm and the particle size of the hydrate produced must be updated regularly. This regular updating may be applied at a less frequent rate than daily measurements (for example monthly).

The actual process control comprises the following phases:

b1) A daily measurement of X1 μm in the slurry at a particular point in the precipitation system, in order to complete the first particle size time diagram represented by the curve $Y = \%X1(t)$.

b2) A daily measurement of X2 μm in the slurry at a particular point in the precipitation system, in order to complete the first particle size time diagram represented by the curve $Y = \%X2(t)$.

b3) Regular updating (for example monthly) of the empirical relation R between the two particle size time diagrams and the definition of trigger thresholds of $X_1 \mu\text{m}$, or updating after an important modification in a process parameter.

b4) Triggering of a corrective action in the slurry at the beginning of the precipitation when the measured value of $X_1 \mu\text{m}$ reaches one of the thresholds defined in b3).

This corrective action is preferably a modification to the solid content in the slurry in the first agglomeration tank. If

there are too many fines,

is reduced by introducing a small aliquot of the pregnant aluminate liquor into the first agglomeration tank. If

pregnant

aluminate liquor into the agglomeration tank is reduced and feed tanks is increased.

As for the preparatory step, empirical relations are determined starting from daily particle size measurements made on the hydrate.

As for the preparatory step, the daily rate is not necessarily daily, but is sufficiently frequent to be able to produce useable time diagrams. Trigger thresholds on the

curve are also deduced from the particle size time diagram; they take account of the uncertainty of the measurement of the maximum authorized variation interval on values of

X2 μm , and the stability of the efficiency of the hydrate classification system.

For relatively low solid content

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This may be done using instruments that diffract laser beams and make mass determinations (Malvern Mastersizer, Cilas, etc.).

10 But in order to increase productivity, much higher solid content must be achieved, comparable to those achieved in European type processes, in other words greater than 700 g/liter.

However, solid content in feed

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the need for a low value of X1. When the solid content is high, a

longer time is necessary to correct particle size disturbances; therefore, it is necessary to have a greater time shift τ ; and this time shift is

20 proportional to the difference between X1 and X2.

In this case,

a lower value (down to 1.5 μm). When X1 becomes low, it

25 becomes necessary to use a celloscopic measurement (COULTER or ELZONE) that determines counts rather than mass. These measurements are more difficult, but the economic consequences are negligible.

30 Productivity can also be increased by increasing the caustic content of the aluminate liquor. The applicant has observed that this method of controlling the particle size can be applied very well on

industrial installations with concentrations reaching 160 g of Na_2O / liter.

Concerning the corrective action, it is also recommended that an empirical relation should be set up in advance to quantify the effects of the said action, for example during the preparatory phase. Thus, in order to quantify the effects of the modification to the solid content in the first agglomeration tank, the first step will be to establish the actual relation between the said solid content and the proportion of destroyed fines.

Embodiments of the invention - Examples

The embodiment of the invention will be better understood from the following description of a number of examples.

Figures 1 and 2 show the part of the Bayer circuit corresponding to the precipitation phase, the precipitation being of the American type with a preliminary agglomeration step.

Figure 1 illustrates the first example typical of prior art.

Figure 3 illustrates subsequent examples describing two embodiments of this invention.

These embodiments are described in examples 2 and 3. To simplify the presentation, we have illustrated the classification phase all conventional classification devices in example 1. In fact, and particularly with solid content,

could select additional or replacement systems such as cyclones or filters.

Example 1 (Prior art)

The pregnant aluminate liquor **1** enters the precipitation circuit at a temperature of about 75°C, enters the first agglomeration tank **A**. It has a caustic concentration of 130 g of Na₂O/ liter.

The tertiary seed **9**, composed essentially of fine and ultrafine particles, is added into the first agglomeration tank **A** and is mixed with pregnant liquor. The resulting slurry **2** passes through a sequence of agglomeration tanks such that practically all fines and ultrafines have disappeared after an average residence time of about 5 hours. During the agglomeration phase, the solid content in the slurry has increased from 20 g aluminate/ liter to about 30 g aluminate/ liter.

At the exit from the agglomeration series, the slurry **3** is added into the first feed tank **N** with the secondary seed **8**, and the addition increases the solid content by 30 g aluminate/ liter. The new slurry **4** passes through a sequence of feed tanks with an average residence time of about 20 hours, and cooling by about 5°C. At the exit from the slurry **5**, called "pump-off",

liter. By measuring of this slurry **5** at the exit from **M1**, the particle size quality of the production hydrate can be estimated so that an optimum variation interval can be defined for this 45 µm. Under the

conditions in the example,

will

give a good quality "metallurgical" alumina.

The slurry **5** at the exit from ... is then added into the first classifier tank **PT**. The overflow **100** from the first classifier **PT** produces production hydrate and the overflow **6** that has a solid content of 100 g aluminate liter, is added into a second classifier tank **ST**. The underflow from the second classifier tank **ST** acts as a secondary seed **8** that is ...

N and the overflow **7**, which then has a solid content of only 20 g/ liter, is sent to a third classifier tank **TT**. The overflow **10** from the third classifier tank is the spent aluminum liquor that is injected as the bauxite green liquor at the beginning of the Bayer cycle, after concentration by evaporation and addition of soda. The overflow **9** from the third classifier tank is added as the tertiary seed into the first agglomeration tank **A** after filtration and washing.

Example 2: Precipitation according to the invention with an average solid content in the rotating ... hydrate

The pregnant aluminate liquor **1** that enters the precipitation circuit at a temperature of about 75°C, is separated into two aliquots, the first aliquot **1a** representing about one third of the total liquor being added into the first agglomeration tank **A**, and the

second aliquot **1n** being added into the first feed tank **N**. The caustic concentration in the pregnant aluminate liquor **1** is 130 g of Na_2O / liter.

The tertiary seed **9a**, composed essentially of fine and ultrafine particles, is added into a first agglomeration tank **A** after filtration and partial or complete washing, and is mixed with the pregnant liquor. The resulting suspension **2** follows a sequence of agglomerating tanks such that a predefined proportion of fines and ultrafines has disappeared after an average residence time of 5 hours. During the agglomeration phase, the quantity of hydrate is increased by 10 g of aluminate entering the workshop (1a and 1n).

The slurry **3** at the exit from the agglomeration series is added into the first feed tank **N** with the second aliquot **1n** of pregnant aluminate liquor, the rest of the **3a** washed or **3b** and the secondary seed **8**, the addition of which increases the solid content by 220 g aluminate liter. The new slurry **4** follows a series of feed tanks with an average residence time of 20 hours and cooling of 5°C . At the exit from the crystal growth, the slurry **5**

liter.

The slurry **5** at the exit is added into a first classifier tank **PT**. The underflow **100** from the first classifier **PT** supplies the production hydrate, and the overflow **6** which has a solid content of 250 g aluminate liter is added into a second classifier tank **ST**. The underflow from the second classifier tank **ST** acts as a

secondary seed **8** that is

N and the overflow **7**, which then only has a solid content of 30 g/ liter, is sent to the third
5 classifier tank **TT**.

A measurement **M1** of the **45** μm ,
and a measurement **M2** of the **20** μm ,
are made in the slurry every day at

using a laser diffraction
10 apparatus.

Observations of the particle size quality of the hydrate produced can be used to define the authorized variation interval on values of **45** μm , and the target set value **C** on the **20** μm is defined, by means of the empirical
15 relation defined during the preparation phase and continually updated afterwards.

Depending on the difference between **M2** and the value of the set value **C** defined in advance to
20 guarantee the particle size quality of the product and the differences **M2 - C** obtained in the previous days, the quantity of fines to be agglomerated in addition to or less than the previous day, are determined.

During the preparation phase, the relation between
25 the solid content in the agglomeration phase and the proportion of destroyed fines was determined. This relation is used to fix the aliquot **1a** used in the agglomeration. This aliquot **1a** fixes the solid content in the agglomeration tanks and therefore the change
30 required for destruction of the fines.

Furthermore, starting from measurements **M1** and **M2** made on previous days, the relation between the set value **C** and the required level **M1** for

45 μm , and secondly the relation between the solid content and fines destroyed in the agglomeration, are adjusted.

5 **Example 3: Precipitation according to the invention with a high solid content in the rotating**
hydrate

The pregnant aluminate liquor **1** arriving in the
 10 precipitation circuit at a temperature of about 75°C ,
 is separated in two aliquots, the first **1a** representing
 about half of the total liquor being added into the
 first agglomeration tank **A**, the second **1n** being added
 into the first feed tank **N**. The caustic concentration
 15 in the pregnant liquor **1a** is 130 g of Na_2O / liter.

The filtered tertiary seed **9**, composed essentially
 of fine and ultrafine particles, is added into the
 agglomeration step **A** and mixed with the fraction 1a of
 pregnant liquor. The resulting slurry **2** stays in the
 20 agglomeration phase for about 5 hours. The proportion
 between the quantity of tertiary seed and the flow of
 liquor 1a is adjusted such that a predefined proportion
 of fines and ultrafines disappears. The quantity of
 hydrate during the agglomeration phase is increased by
 25 15 g of aluminate entering in the workshop

(**1a** and **4n**).

At the exit from the agglomeration series, the
 slurry **3** is added into the first feed tank **N** and with
 the second aliquot **1n** of pregnant aluminate liquor and
 30 the secondary seed **8**, the addition of which increases
 the solid content by 840 g aluminate liter. The
 new slurry **4** passes through a series of feed tanks with

an average residence time of 18 hours and cooling by 10°C. At the exit from the

about 1000 g aluminate liter.

5 At least one measurement **M1** of 45 µm is made every day at this location using a laser diffraction apparatus, and a measurement **M2** of 1.5 µm is made with an ELZONE counter.

10 The slurry **5** at the exit from the crystal growth is added into a first classifier tank **PT**. The underflow **100** from the first classifier **PT** supplies the production hydrate and the overflow **6**, that has a solid content of 870 g/ liter, is
15 added into a second classifier tank **ST**. The underflow from the second classifier tank **ST** is used as a secondary seed **8** that is injected at the beginning of the crystal growth **N** after filtration and the overflow **7**, that has a solid content that no longer exceeds 30
20 g/ liter, is sent to the third classifier tank **TT**.

The process for monitoring and controlling the particle size of the hydrate in the slurry at pump-off is identical to that described in example 2.

Advantages of the process according to the invention

- Particle size fluctuations related to the increase in the inertia of the system originating from the increase in solid contents are avoided.
- The productivity of liquors can thus be increased:
 - by controlling crystallization at high solid contents without endangering the quality of the alumina produced,
 - by adjusting the pump-off particle size to the maximum level compatible with quality requirements and the production classification system.